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# CHEMICAL RESISTANCE OF ZINC-BEARING GLASS-CERAMIC GLAZE FOR QUARTZ GLASS CERAMICS

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The chemical resistance of a zinc-bearing glass-ceramic glaze intended to protect refractory products made of quartz glass ceramics from alkali media is investigated. The water and acid resistance of the glaze exceeds the analogous parameters of traditional glaze glasses. The alkali resistance of quartz glass ceramics coated by the glass-ceramic glaze increases more than 4 times.

Quartz glass ceramics are high-silica materials produced by sintering milled quartz glass or various types of amorphous silica [1 – 3]. Owing to the high thermomechanical and electroengineering characteristics, radiation permeability, technological efficiency, and low cost, quartz glass ceramics finds wide application in spacecraft engineering, nuclear power, and metallurgy. Recently, the application areas of this material have been extended to refractories in the chemical and glass industry sectors. In particular, there has been practical experience in using quartz glass ceramics to produce refractories for glass-melting furnaces. However, wide use of quartz glass-ceramic refractories is limited due to the low alkali resistance of this material, especially at elevated temperatures.

The intensity of chemical corrosion of a refractory in aggressive media is primarily determined by the chemical nature of the refractory and the medium interacting with it. Qualitatively, the properties of quartz glass ceramics are correlated with the quartz glass and exhibit high resistance to reactants of group I (water, acid solutions and acids) and also to liquid metals and gases. In contact with reactants of group II (alkalis, fluoric and phosphoric acids and their salts), the material undergoes intense chemical corrosion, up to complete destruction [4]. A promising method for improving the corrosion resistance, service reliability, and durability of quartz glass-ceramic refractories operating in contact with high-temperature alkali media is the deposition of chemically resistant glaze coatings.

The complexity of glazing quartz glass ceramics, which is characterized by low thermal expansion, is that its TCLE is hard to coordinate with the TCLEs of most known glazes. A substantial difference between the TCLEs of the glaze and the substrate generates numerous defects in the coating and decreases the strength of its adhesion to the substrate [5, 6]. A promising line for solving this problem is to develop glass-ceramic glazes, whose phase composition is represented by crystalline phases with low thermal expansion, which provides for a significant decrease in the thermal expansion of the coating in general and a better coordination with the substrate.

Researchers at the D. I. Mendeleev Russian Chemical Engineering University have developed a zinc-bearing glass-ceramic glaze for quartz glass ceramics, whose chemical composition is in the willemite range of the $K_2O – ZnO – TiO_2 – SiO_2$ system [7]. The fritted vitreous glaze is applied to the surface of quartz glass ceramics by immersion or casting and is fired according to a two-stage schedule with exposures at 1280°C (stage I, spreading of glaze) and 1050 – 1150°C (stage II, crystallization of coating). The thickness of the coating layer is 160 – 200 μm. A finely dispersed glass-ceramic volume structure is formed in the glaze under firing, consisting of willemite crystals and willemite-based solid solutions, zircon titanates, rutile, and a residual vitreous phase. The glaze coating forms strong adhesion to the substrate without crackle, flaking, or other defects.

The present work shows the results of studying chemical resistance of the specified glass-ceramic glaze in various media. The substrate for depositing the glaze was glass ceramics produced by the Simvol Company (Vladimir Region). The chemical resistance of vitreous frit and crystallized glaze were determined by the granular method based on the weight loss in material samples, and the chemical resistance of the glass-ceramic coating was determined by the mold surface method based on weight losses in quartz glass-ceramic samples after boiling in water, acids, and in a caustic soda solution. For reference purposes the behavior of unglazed glass ceramics in reaction with water, alkali, and acid media was evaluated.

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**TABLE 1**

| Medium* | Weight loss, % | | |
|---|---|---|---|
| | vitreous frit | crystallized glaze | quartz glass ceramics |
| $H_2O$ | 0.135 ± 0.05 | 0.097 ± 0.05 | 5 ± 1 (increased weight) |
| 2 N HCl | 0.5 ± 0.05 | 0.1 ± 0.05 | 5 ± 1 (increased weight) |
| 2 N NaOH | 8 ± 1 | 5 ± 1 | Dissolution of sample |

* Boiling duration 15 min.

**TABLE 2**

| Chemical reactant* | Medium temperature, °C | Quartz glass ceramics | |
|---|---|---|---|
| | | unglazed | glazed |
| $H_2O$ | 100 | No reaction | No reaction |
| 2 N $H_2SO_4$ | 100 | The same | Very weak reaction |
| HF | 20 | Intense reaction | Medium-intensity reaction |
| 2 N NaOH | 100 | Very intense reaction | Weak reaction |

* Treatment duration in all cases was 1 h.

Experimental data (Table 1) indicate that the developed glaze composition has sufficiently high chemical strength in water (hydrolytic class II) and in hydrochloric acid, exceeding the chemical resistance of normal glaze glasses (hydrolytic class III). It is difficult to compare the water and acid resistance of glaze and quartz glass ceramics, since when the latter reacts with the specified media, the sample weight increases owing to absorption of a liquid medium by the pores of the material. However, considering the very high resistance of quartz glass and materials based on it to reactants of group I, it can be assumed that these properties are better in glass ceramics than in glaze. In contrast, the alkali resistance of the glass-ceramic glaze significantly exceeds that of quartz glass ceramics. Thus, after boiling in an alkaline solution for 15 min a quartz glass-ceramic sample completely dissolves, whereas the weight loss of the glass-ceramic glaze does not exceed 5 – 6%.

The intensity of the reaction of unglazed and glazed quartz glass ceramics with aggressive media (Table 2) correlates with data on chemical resistance of materials. It is noted that boiling unglazed and glazed samples in reactants of group I (water and acid, except for fluoric acid) does not produce significant chemical corrosion of the surface. Reactants of group II (alkalis, fluoric acids) produce very intense corrosion of the surface of unglazed glass ceramics, which is expressed in the formation of depressions, craters, and gradual pickling of the surface layers of samples. The glazed samples of quartz glass ceramics to a much lesser degree are susceptible to the corroding effect of these media.

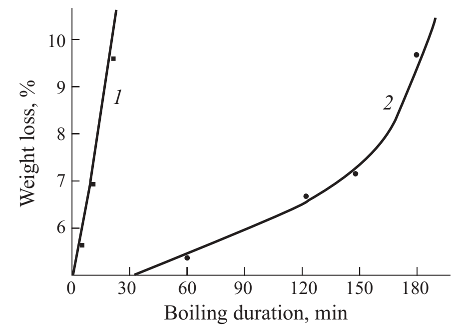


**Fig. 1.** Chemical corrosion of unglazed (*1*) and glazed (*2*) quartz glass ceramics in 2 N NaOH in boiling.

The kinetic curves of reaction of unglazed and glazed quartz glass ceramics with an alkali solution in boiling are shown in Fig. 1. It can be seen that unglazed quartz glass ceramic is susceptible to intense corrosion already in the initial stages of reaction. Even after 5 min of boiling the weight loss is 1%. The first symptoms of reaction of a glazed sample with an alkaline medium are registered only after a 45-min exposure in a boiling solution. A comparable weight loss for the unglazed sample is attained 4 – 5 times faster than for the glazed sample, i.e., the alkali resistance of quartz glass ceramics after glazing grows more than 4 times.

The shape of the dependences represented in Fig. 1 confirms that in both cases reaction with an alkaline medium proceeds similarly to the mechanism of reaction of silicate materials with group II reactants: dissolution of the structure-forming silicon-oxygen skeleton of the material without the formation of protective layers [8].

In the case of an unglazed sample, this is indicated by a linear dependence of weight loss $L$ on the reaction duration $\tau$:

$$L_{\mathrm{cer}} = A_{\mathrm{cer}}\,\tau,$$

where $A$ is a constant.

In the case of a glazed sample a more complex dependence is registered, in which several segments can be identified: at first (for about 30 min) there is no visible reaction with the alkali solution; next, the primary phase of reaction is observed, i.e., the first linear segment (up to 150 – 160 min), then the second stage of reaction, i.e., the second linear segment (after 180 – 190 min). These linear segments are connected by a smooth nonlinear curve segment. Similarly to the case of the unglazed sample, both linear segments of the kinetic dependence are described by linear functions:

$$L_{\mathrm{gl(1)}} = B_1 + A_{\mathrm{gl(1)}}\,\tau;$$

$$L_{\mathrm{gl(2)}} = B_2 + A_{\mathrm{gl(2)}}\,\tau,$$

where $A$ and $B$ are constants.

The constants $A_{\mathrm{cer}}$, $A_{\mathrm{gl(1)}}$, and $A_{\mathrm{gl(2)}}$ that characterize the rate of reaction were calculated based on the slope of the li-

near segments: $A_{cer} = 0.2$ %/min; $A_{gl(1)} = 0.057$ %/min; $A_{gl(2)} = 0.22$ %/min.

Comparing constants $A$ of the considered dependences, it is worth noting that $A_{gl(1)} \ll A_{cer}$ and $A_{gl(2)} \approx A_{cer}$. This makes it possible to interpret the obtained results as follows. In the case of unglazed quartz glass ceramics, reaction with the alkali solution proceeds very intensely at a constant rate ($A_{cer} = 0.2$ %/min). In the case of the glazed sample, in the first stage the alkali solution reacts with glass-ceramic glaze at a rate approximately 4 times lower ($A_{gl(1)} = 0.057$ %/min). However, with time the glaze layer gradually becomes corroded, the quartz glass ceramics under this layer is bared, and the intensity of the reaction starts growing.

The nonlinear curve segment (reaction duration 150 – 190 min) correlates with the period when certain sites of the glaze coating of minimum thickness dissolve and the quartz glass ceramics underneath become bared and immediately enter into an intense reaction with the alkali solution. The rate of reaction with the medium in this segment is an averaged value of the reaction rates of glaze and quartz glass ceramics and keeps growing (a nonlinear correlation) as a consequence of ever increasing dissolution of the glaze coating and baring of the surface of the quartz glass ceramics. The second stage of reaction (starting with 180 – 190 min) correlates with the full dissolution of the entire glaze coating and reaction of unprotected quartz glass ceramic with the alkali solution. This is corroborated by virtually equal values of $A_{cer}$ and $A_{gl(2)}$, i.e., virtually equal reaction rates of unglazed and glazed quartz glass-ceramic samples within the specified period.

Thus, it is experimentally confirmed that zinc-bearing glass-ceramic glaze provides protection for quartz glass ceramics from the effect of alkali media. This is due, on the one hand, to a high concentration of zinc and titanium oxides in the glaze composition, which have a strong positive effect on the chemical resistance of silicate glasses, and on the other hand, to the presence of crystalline phases that have higher chemical resistance than glass of a respective composition.

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